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(54) Title: BLENDS OF ELASTOMER BLOCK COPOLYMER AND ALIPHATIC ALPHA-OLEFIN/MONOVINYLDENE AROMATIC MONOMER AND OR HINDERED ALIPHATIC VINYLIDENE MONOMER INTERPOLYMER

(57) Abstract

A thermoplastic elastomeric blend composition comprising: (A) from 99 to 1 weight percent of a styrenic block copolymer; and (B) from 1 to 99 weight percent of an interpolpolymer of (1) at least one aliphatic α -olefin and (2) at least one vinylidene aromatic monomer or (3) a combination of at least one vinylidene aromatic monomer and at least one hindered aliphatic vinylidene monomer, wherein said vinylidene aromatic monomer is present in an amount of from 0.5 to 45 mole % or from 17 to 65 mole % in said interpolpolymer, and fabricated articles made from such composition.

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BLEND OF ELASTOMER BLOCK COPOLYMER AND ALIPHATIC ALPHA-
OLEFIN MONOVINYLLIDENE AROMATIC MONOMER AND/OR HINDERED ALIPHATIC
VINYLLIDENE MONOMER INTERPOLYMER

5 This invention relates to a thermoplastic elastomeric blend composition comprising an elastomer block copolymer and an α -olefin/monovinylidene aromatic monomer and/or hindered aliphatic vinylidene monomer interpolymer, and to fabricated articles made therefrom.

10 Elastomer block copolymers of polystyrene and rubber are widely used in the industry, frequently for impact modification of thermoplastic resins and engineering thermoplastics or for compatibilization of different types of resins. The class of elastomer saturated rubber block copolymers, such as styrene-
15 ethylene/butene-styrene block copolymers S-EB-S, however, is expensive to produce and difficult to process. The class of unsaturated rubber block copolymers such as Styrene-Butadiene-Styrene (SBS) is susceptible to degradation. Blends of polymer components not readily miscible with these block copolymers, such as conventional
20 polyethylenes, can exhibit inferior mechanical properties, especially elastomeric retention such as permanent tensile set after elongation.

It would be desirable to provide either lower cost or more durable blends of these block copolymers by adding a polymeric component that does not significantly decrease the required
25 performance properties. It would be further desirable to provide blends of these block copolymers and a polymeric component thereby maintaining or improving the performance of these block copolymers while providing low haze blends. It would also be desirable to maintain a low value for hardness as desired for applications
30 requiring flexibility such as sheet, film or tubing. It would also be desirable to maintain a high level of ultimate tensile properties to enhance the strength properties of the blends. Finally it would also be desirable to maintain a high level of % stress relaxation to enhance the surface conformity of the blends especially in
35 applications requiring covering of a surface.

According to the present invention there is provided a thermoplastic elastomeric blend composition comprising:

(A) from 99 to 1 weight percent of a styrenic block copolymer; and

40 (B) from 1 to 99 weight percent of an interpolymer of (1) at least one aliphatic α -olefin and (2) at least one vinylidene aromatic

monomer or a combination of at least one vinylidene aromatic monomer and at least one hindered aliphatic vinylidene monomer, wherein said vinylidene aromatic monomer is present in an amount of from 10 to 15 mole % to from 10 to 45 mole % in said interpolymer.

In yet another aspect, the present invention provides a fabricated article made from such a thermoplastic elastomeric blend composition.

In yet another aspect, the present invention comprises an adhesive or adhesive formulation or a sealant formulation containing the aforementioned blends.

The term "interpolymer" is used herein to indicate a polymer wherein at least two different monomers are polymerized to make the interpolymer.

The term "hydrocarbyl" means any aliphatic, cycloaliphatic, aromatic, aryl substituted aliphatic, aryl substituted cycloaliphatic, aliphatic substituted aromatic, or cycloaliphatic substituted aromatic groups. The aliphatic or cycloaliphatic groups are preferably saturated. Likewise, the term "hydrocarbyloxy" means a hydrocarbyl group having an oxygen linkage between it and the carbon atom to which it is attached.

The term "monomer residue" means that portion of the polymerizable monomer molecule which resides in the polymer chain as a result of being polymerized with another polymerizable molecule to make the polymer chain.

The term "substantially random" in the substantially random interpolymer comprising an α -olefin and a vinylidene aromatic monomer or hindered aliphatic vinylidene monomer as used herein means that the distribution of the monomers of said interpolymer can be described by the Bernoulli statistical model or by a first or second order Markovian statistical model, as described by J. C. Randall in POLYMER SEQUENCE DETERMINATION, Carbon-13 NMR Method, Academic Press New York, 1977, pp. 71-78. Preferably, the substantially random interpolymer comprising an α -olefin and a vinylidene aromatic monomer does not contain more than 15 percent of the total amount of vinylidene aromatic monomer in blocks of vinylidene aromatic monomer of more than 3 units. More preferably, the interpolymer was not characterized by a high degree of either isotacticity or syndiotacticity. This means that in the carbon-13 NMR spectrum of the substantially random interpolymer the peak areas corresponding to the main chain methylene

and methine carbons representing either head head sequences or racemic head sequences should not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

The term "block copolymer" as used herein to mean elastomers having at least one block segment of a hard polymer unit and at least one block segment of a rubbery polymer unit. However, the term is not intended to include thermoplastic ethylene interpolymers which are, in general, random polymers. Preferred block copolymers contain hard segments of styrenic type polymers in combination with saturated or unsaturated rubber monomer segments. The structure of the block copolymers useful in the present invention is not critical and can be of the linear or radial type, either diblock or triblock, or any combination of thereof.

Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 1 unit between any lower value and any higher value. As an example, if it is stated that the amount of a component or a value of a process variable such as, for example, temperature, pressure, time and the like is, for example, from 1 to 80, preferably from 20 to 60, more preferably from 30 to 70, it is intended that values such as 15 to 65, 22 to 68, 43 to 61, 30 to 32 etc. are expressly enumerated in this specification. For values which are less than one, the unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

Suitable unsaturated block copolymers include those represented by the following formulas:

Formula I $A-B-R(-B-A)_n$ or

Formula II $A_x-(BA-)_y-BA$

wherein each A is a polymer block comprising a monovinylidene aromatic monomer, preferably styrene, and each B is a polymer block comprising a conjugated diene, preferably isoprene or butadiene, and optionally a monovinylidene aromatic monomer, preferably styrene; R is the remnant of a multifunctional coupling agent; n is an integer from 1 to 5; x is zero or 1; and y is a real number from zero to 4.

The preparation of the block copolymers useful herein is not the subject of the present invention. Methods for the preparation of such

block copolymers are known in the art. Suitable catalysts for the preparation of useful block copolymers with unsaturated rubber monomer units include lithium based catalysts and especially lithium-alkyls. U.S. Pat. No. 4,199, 411 describes suitable methods for hydrogenation of block copolymers with unsaturated rubber monomer units to form block copolymers with saturated rubber monomer units. The structure of the polymers is determined by their methods of polymerization. For example, linear polymers result by sequential introduction of the desired rubber monomer into the reaction vessel when using such initiators as lithium-alkyls or dilithiostilbene and the like, or by coupling a two segment block copolymer with a difunctional coupling agent. Branched structures, on the other hand, may be obtained by the use of suitable coupling agents having a functionality with respect to the block copolymers with unsaturated rubber monomer units of three or more. Coupling may be effected with multifunctional coupling agents such as dihaloalkanes or alkenes and divinyl benzene as well as with certain polar compounds such as silicon halides, siloxanes or esters of monohydric alcohols with carboxylic acids. The presence of any coupling residues in the polymer may be ignored for an adequate description of the block copolymers forming a part of the composition of this invention.

Suitable block copolymers having unsaturated rubber monomer units includes, but is not limited to, styrene-butadiene (SB), styrene-isoprene (SI), styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), α -methylstyrene-butadiene- α -methylstyrene and α -methylstyrene-isoprene- α -methylstyrene.

The styrenic portion of the block copolymer is preferably a polymer or interpolymers of styrene and its analogs and homologs including α -methylstyrene and ring-substituted styrenes, particularly ring-methylated styrenes. The preferred styrenics are styrene and α -methylstyrene, and styrene is particularly preferred.

Block copolymers with unsaturated rubber monomer units may comprise homopolymers of butadiene or isoprene or they may comprise copolymers of one or both of these two dienes with a minor amount of styrenic monomer.

Preferred block copolymers with saturated rubber monomer units comprise at least one segment of a styrenic unit and at least one segment of an ethylene-butene or ethylene-propylene copolymer. Preferred examples of such block copolymers with saturated rubber monomer units include styrene/ethylene-butene copolymers,

styrene-ethyl-methacrylate copolymers, styrene-ethyl-methacrylate-styrene-ethyl-methacrylate copolymers, styrene-ethyl-methacrylate-styrene-ethyl-methacrylate copolymers, styrene-ethyl-methacrylate-styrene-ethyl-methacrylate copolymers.

Hydrogenation of block copolymers with unsaturated rubber monomer units is preferably effected by use of a catalyst comprising the reaction products of an aluminum alkyl compound with nickel, or cobalt, carboxylates or alkoxides under such conditions as to substantially completely hydrogenate at least 50 percent of the aliphatic double bonds while hydrogenating no more than 10 percent of the styrenic aromatic double bonds. Preferred block copolymers are those where at least 50 percent of the aliphatic double bonds are hydrogenated while less than 5 percent of the aromatic double bonds are hydrogenated.

The proportion of the styrenic blocks is generally between 5 and 45 percent by weight of the total weight of the block copolymer. Preferably, the block copolymers contain from 10 to 35 weight percent of styrenic block segments and from 20 to 45 weight percent of rubber monomer block segments, based on the total weight of the block copolymer.

The average molecular weights of the individual blocks may vary within certain limits. In most instances, the styrenic block segments will have number average molecular weights in the range of 5,000 to 125,000, preferably from 7,000 to 60,000 while the rubber monomer block segments will have average molecular weights in the range of 10,000 to 300,000, preferably from 30,000 to 150,000. The total average molecular weight of the block copolymer is typically in the range of 25,000 to 450,000, preferably from 35,000 to 200,000.

Further, the various block copolymers suitable for use in the present invention may be modified by graft incorporation of minor amounts of functional groups, such as, for example, maleic anhydride by any of the methods well known in the art.

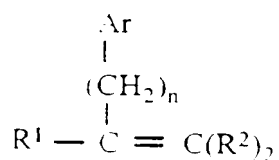
Block copolymers useful in the present invention are commercially available, such as, for example, supplied by Shell Chemical Company under the designation of KRATONTM and supplied by Dexco Polymers under the designation of VECTORTM.

Blend component B for the polymer blend composition of the present invention include, but are not limited to, substantially random interpolymers prepared by polymerizing one or more α -olefin monomers with one or more vinylidene aromatic monomers and/or one or

more hindered aliphatic or cycloaliphatic vinylidene monomers, and optionally with other polymerizable ethylenically unsaturated monomers.

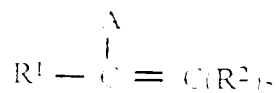
Suitable α -olefin monomers contained in the blend component B include, for example, aliphatic and cycloaliphatic α -olefins having from 2 to 16 carbon atoms, and preferably α -olefins having from 2 to 8 carbon atoms. Most preferably, the aliphatic α -olefin of blend component B comprises ethylene or propylene, preferably ethylene, optionally together with one or more other α -olefins having from 3 to 8 carbon atoms, such as ethylene and propylene, or ethylene and octene, or ethylene and propylene and octene.

Suitable vinylidene aromatic monomers which can be employed to prepare the interpolymers include, for example, those represented by the following formula:



wherein R^1 is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; each R^2 is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo, C_{1-4} -alkyl, and C_{1-4} -haloalkyl; and n has a value from zero to 4, preferably from zero to 2, most preferably zero. Exemplary monovinylidene aromatic monomers include styrene, vinyl toluene, α -methylstyrene, t-butyl styrene, chlorostyrene, including all isomers of these compounds. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers include styrene, α -methyl styrene, the lower alkyl- ($\text{C}_1 - \text{C}_4$) or phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-methylstyrene, the ring halogenated styrenes, para-vinyl toluene or mixtures thereof. A more preferred aromatic monovinylidene monomer is styrene.

By the term "hindered aliphatic or cycloaliphatic vinylidene compounds", it is meant addition polymerizable vinylidene monomers corresponding to the formula:



wherein A is a sterically bulky aliphatic or cycloaliphatic substituent (up to 6 carbons, R¹ is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, or phenyl, hydrogen or methyl; each R² is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; or alternatively R¹ and A together form a ring system. By the term "sterically bulky" is meant that the monomer bearing this substituent is normally incapable of addition polymerization by standard Ziegler-Natta polymerization catalysts at a rate comparable with ethylene polymerizations. Preferred hindered aliphatic or cycloaliphatic vinylidene compounds are monomers in which one of the carbon atoms bearing vinylidene unsaturation is tertiary or quaternary substituted. Examples of such substituents include cyclic aliphatic groups such as cyclonexyl, cyclonexenyl, cyclooctenyl, or ring alkyl or aryl substituted derivatives thereof, tert-butyl, norbornyl. Most preferred hindered aliphatic or cycloaliphatic vinylidene compounds are the various isomeric vinyl- ring substituted derivatives of cyclonexene and substituted cyclonexenes, and 5-ethylidene-3-norbornene. Especially suitable are 1-, 3-, and 4-vinylcyclohexene.

The interpolymers of one or more α -olefins and one or more monovinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers employed in the present invention as component B, are substantially random polymers. These interpolymers usually contain from 1 to 65, preferably from 5 to 60, more preferably from 10 to 55 mole percent of at least one vinylidene aromatic monomer and/or hindered aliphatic or cycloaliphatic vinylidene monomer and from 35 to 99, preferably from 40 to 95, more preferably from 45 to 90 mole percent of at least one aliphatic α -olefin having from 2 to 20 carbon atoms.

Preferably, higher molecular weight interpolymer component (B) are used, such as those that possess a number average Mw of greater than 10,000. Also preferably such polymers possess a melt index (I₂), ASTM D-1238 Procedure A, Condition E, of less than 125, more preferably from 1.01 to 100, even more preferably from 0.01 to 25, and most preferably from 0.05 to 5. Also, the substantially random interpolymers have a heat of fusion of less than 50 J/g.

The present invention provides blends of interpolymer components of molecular weight and composition distributions selected to obtain an overall molecular weight and composition distribution which gives enhanced properties or processability.

While preparing the substantially random interpolymers, component 31, as will be described hereinafter, in amount of atactic vinylidene aromatic homopolymer may be formed due to homopolymerization of the vinylidene aromatic monomer at elevated temperatures. In general, the higher the polymerization temperature was, the higher is the amount of homopolymer formed. The presence of vinylidene aromatic homopolymer is in general not detrimental for the purposes of the present invention and may be tolerated. The vinylidene aromatic homopolymer may be separated from the interpolymer, if desired, by extraction techniques such as selective precipitation from solution with a non solvent for either the interpolymer or the vinylidene aromatic homopolymer. For the purpose of the present invention it is preferred that no more than 20 weight percent, preferably less than 15 weight percent based on the total weight of the interpolymers of vinylidene aromatic homopolymer is present.

The substantially random interpolymers may be modified by typical grafting, hydrogenation, functionalizing, or other reactions well known to those skilled in the art. The polymers may be readily sulfonated or chlorinated to provide functionalized derivatives according to established techniques.

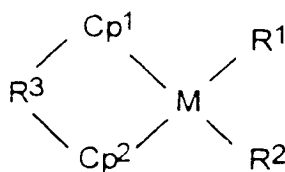
The substantially random interpolymers are prepared by polymerizing a mixture of polymerizable monomers in the presence of metallocene or constrained geometry catalysts.

The substantially random interpolymers can be prepared as described in US Application Serial Number 545,403 filed July 3, 1990 (corresponding to EP-A-0,416,815) by James C. Stevens et al., both of which are incorporated herein by reference in their entirety. Preferred operating conditions for such polymerization reactions are pressures from atmospheric up to 3000 atmospheres and temperatures from -30°C to 200°C. Polymerizations and unreacted monomer removal at temperatures above the autopolymerization temperature of the respective monomers may result in formation of some amounts of homopolymer polymerization products resulting from free radical polymerization.

Examples of suitable catalysts and methods for preparing the substantially random interpolymers are disclosed in U.S. Application Serial No. 08/147,913, filed May 1, 1994, EP-A-014,818; U.S. Application Serial No. 08/147,915, filed May 1, 1994, EP-A-014,819; U.S. Application Serial No. 08/147,916, filed May 1, 1994, EP-A-014,820; U.S. Application Serial No. 08/147,917, filed May 11, 1994; as well as U.S. Patents 5,374,775; 5,386,867; 5,364,811; 5,130,880; 5,133,193; 5,311,100; 5,187,121; 5,381,733; 5,374,696; and 5,399,839 all of which patents and applications are incorporated herein by reference.

The substantially random α -olefin/vinylidene aromatic interpolymers can also be prepared by the methods described by John G. Bradtute et al., U.S. Pat. 4,800,400; by R. E. Pannell, Exxon Chemical Patents, Inc., U.S. Pat. 4,850,777 and in Elastics Technology, Vol. 17, September 1993, all of which are incorporated herein by reference in their entirety.

The substantially random α -olefin/vinylidene aromatic interpolymers can also be prepared by the methods described in JP 07/279231 employing compounds shown by the general formula



where Cp^1 and Cp^2 are cyclopentadienyl groups, indenyl groups, fluorenyl groups, or substituents of these, independently of each other; R^1 and R^2 are hydrogen atoms, halogen atoms, hydrocarbon groups with carbon numbers of 1-12, alkoxy groups, or aryloxy groups, independently of each other; M is a group IV metal, preferably Zr or Hf, most preferably Cr; and R^3 is an alkylene group or silanediyl group used to cross-link Cp^1 and Cp^2 .

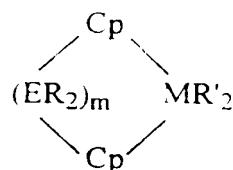
Also suitable are the substantially random interpolymers which possess at least one α -olefin/vinyl aromatic/vinyl aromatic/ α -olefin tetrad disclosed in a copending application by Francis J. Timmers et al. filed on the same date as this application. These interpolymers contain additional signals with intensities greater than three times the peak to peak noise. These signals appear in the chemical shift range 43.70-44.25 ppm and 38.0-38.6 ppm. Specifically, major peaks are observed at 44.1, 43.9 and 38.2 ppm. A proton test NMR experiment indicates that the signals in the chemical shift region 43.70-44.25

ppm are methine carbons and the signals in the region 40.0-45.0 ppm are methylene carbons.

In order to determine the carbon-13 NMR chemical shifts of these interpolymers, the following procedure and conditions are employed. A five to ten weight percent polymer solution is prepared in a mixture consisting of 70 volume percent 1,1,2,2-tetrachloroethane-*g* and 30 volume percent 0.10 molar chromium triisobutyrate in 1,2,4-trichlorobenzene. NMR spectra are acquired at 130°C using an inverse gated decoupling sequence, a 90° pulse width and a pulse delay of five seconds or more. The spectra are referenced to the isolated methylene signal of the polymer assigned at 30.000 ppm.

It is believed that these new signals are due to sequences involving two head-to-tail vinyl aromatic monomer preceded and followed by at least one α -olefin insertion, for example, in ethylene/styrene/styrene/ethylene tetrads wherein the styrene monomer insertions in said tetrads occur exclusively in a 1,3 (head to tail) manner. It is understood by one skilled in the art that for such tetrads involving a vinyl aromatic monomer other than styrene and an α -olefin other than ethylene that the ethylene/vinyl aromatic monomer/vinyl aromatic monomer/ethylene tetrad will give rise to similar carbon-13 NMR peaks but with slightly different chemical shifts.

These interpolymers are prepared by conducting the polymerization at temperatures of from -30°C to 250°C in the presence of such catalysts as those represented by the formula



wherein: each Cp is independently, each occurrence, a substituted cyclopentadienyl group π -bound to M; E is C or Si; M is a group IV metal, preferably Zr or Hf, most preferably Zr; each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to 30 preferably from 1 to 20 more preferably from 1 to 10 carbon or silicon atoms; each R' is independently, each occurrence, H, halo, hydrocarbyl, hydrocarbyloxy, silahydrocarbyl, hydrocarbylsilyl containing up to 30 preferably from 1 to 20 more preferably from 1 to 10 carbon or silicon atoms or two R' groups together can be a C₃₋₁₀ hydrocarbyl substituted 1,3-butadiene; m

to a low and relatively uniform level in the presence of an activating treatment. Additionally, a more pronounced inter-subject variability was observed for the low-dose treatment group, as indicated by the larger error bars.



wherein each R is independently, each occurrence, H, hydrocarbyl, silanohydrocarbyl, or organosilyl, containing up to 30 preferably from 1 to 20 more preferably from 1 to 11 carbon or silicon atoms or two R groups together form a divalent derivative of such group. Preferably, R independently each occurrence is including where appropriate all isomers hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, phenyl, or silyl, or where appropriate two such R groups are linked together forming a fused ring system such as indenyl, fluorenyl, tetrahydronaphenyl, tetrahydrofluorenyl, or octahydrofluorenyl.

Particularly preferred catalysts include, for example, racemic-
dimethylsilanediy[(2-methyl-4-phenylindenyl)]zirconium dichloride,
racemic-(dimethylsilanediy[(2-methyl-4-phenylindenyl)]zirconium 1,4-
diphenyl-1,3-butadiene, racemic- dimethylsilanediy[(2-methyl-4-
phenylindenyl)]zirconium di- C_3H_5 alkyl, racemic-(dimethylsilanediy[(2-
methyl-4-phenylindenyl)]zirconium di- C_3H_5 alkoxide, or any combination
thereof. Also included are the titanium-based catalysts, (N-(1,1-
dimethylethyl)-1,1-dimethyl-1-(1,2,3,4,5- η)-1,3,6,7-tetrahydro-s-
indacen-1-yl)silaniminato α - β -N,titanium dimethyl; (1-indenyl)(tert-
butylamido)dimethylsilane titanium dimethyl; β -tert-
butyl(1,2,3,4,5- η)-1-indenyl, tert-butylamido) dimethylsilane
titanium dimethyl; and α -3-iso-propyl(1,2,3,4,5- η)-1-indenyl)(tert-
butyl amido)dimethylsilane titanium dimethyl, or any combination
thereof.

Further preparative methods for the interpolymer blend component B) of the present invention have been described in the literature. Longo and Grassi (Makromol. Chem., Volume 191, pages 2387 to 2396 (1990)) and D'Anniello et al. (Journal of Applied Polymer Science, Volume 58, pages 1701-1706 (1995)) reported the use of a catalytic system based on methylalumoxane MAO and cyclopentadienyltitanium trichloride ($CpTiCl_3$) to prepare an ethylene-styrene copolymer. Xu and Lin (Polymer Preprints, Am.Chem.Soc., Div. Polym. Chem., Volume 35, pages 686, 687 (1994)) have reported copolymerization using a $TiCl_4/NaCl/Al(iBu)_3$ catalyst to give random copolymers of styrene and

propylene. Journal of Applied Polymer Science, Volume 18, pages 1483-1490 (1974) have described the copolymerization of ethylene and styrene using a $\text{TiCl}_4\text{-NbCl}_5\text{-MgCl}_2\text{-AlEt}_3$ catalyst. The manufacture of α -olefin/vinyl aromatic monomer interpolymers such as propylene/styrene and butene/styrene are described in United States patent number 4,144,947, issued to Mitsui Petrochemical Industries Ltd. All the above methods disclosed for preparing the interpolymer blend components are incorporated herein by reference.

Generally, the blend composition of the present invention comprises from 1 percent to 49 percent, by weight, of the composition, of the substantially random interpolymer of aliphatic α -olefin/vinylidene aromatic monomer component (B) and from 99 to 1 percent, by weight, of the elastomer block copolymer component (A). Preferably, the composition comprises from 1 percent to 50 percent, more preferably from 10 to 45 percent, by weight of the composition, of the interpolymer of aliphatic α -olefin/vinylidene aromatic monomer component (B) and from 50 to 99 percent, more preferably from 50 to 55 percent, by weight of the composition, of the elastomer block copolymer component (A). For the compositions containing at the most 50 weight percent of interpolymer of aliphatic α -olefin/vinylidene aromatic monomer component (B), the compositions maintain a reasonably low Shore A hardness (65 or lower) as well as a fairly constant peak tensile stress, which are desirable properties for elastomeric materials.

For the blend compositions in which the monovinylidene aromatic monomer component of the aliphatic α -olefin/monovinylidene aromatic interpolymer component is present in an amount of from 17 to 65 mole %, preferably from 20 to 65 mole % in said interpolymer, and fabricated articles made from such composition and said interpolymer is present in the blend at a concentration of 25 wt%, then the % stress relaxation of the blends is $\geq 38\%$. Further for the blend compositions in which the monovinylidene aromatic monomer component of the aliphatic α -olefin/monovinylidene aromatic interpolymer component is present in an amount of from 17 to 65 mole %, preferably in an amount of from 20 to 65 mole % and said interpolymer is present in the blend at a concentration of 75 wt%, then the % stress relaxation of the blends is $\geq 65\%$.

Also for the blend compositions in which the monovinylidene aromatic monomer component of the aliphatic α -olefin/monovinylidene aromatic interpolymer component is present in an amount of from 0.5 to 15 mol% and said interpolymer is present in the blend at a

concentration of 15 wt. when the ultimate tensile of the blends is 2
21 MPa. Further, for the blends in which the
monovinylidene aromatic polymer component of the aliphatic α -
olefin monovinylidene aromatic interpolymer component is present in an
amount of from 10 to 15 wt. and said interpolymer is present in the
blend at a concentration of 75 wt. when the ultimate tensile
of the blends is 21 MPa.

Additives such as antioxidants (for example, hindered phenolics
for example, Irganox-1010, phosphites (for example, Irganox-168)),
10 other additives (for example, FIB, nucleated additives, colourants,
pigments, fillers, and the like can also be included in the present
compositions, to the extent that they do not interfere with the
enhanced properties discovered by Applicants.

The compositions of the present invention are compounded by any
15 convenient means, including dry blending the individual components
and subsequently melt mixing, either directly in the extruder or mill
used to make the finished article (for example, the automotive part),
or by pre-melt mixing in a separate extruder or mill (for example, a
Banbury mixer).

20 There are many types of molding operations which can be used to
form useful fabricated articles or parts from the present
compositions, including various injection molding processes (for
example, that described in Modern Plastics Encyclopedia/89, Mid
October 1988 Issue, Volume 65, Number 11, pp. 264-268, "Introduction
25 to Injection Molding" and on pp. 270-271, "Injection Molding
Thermoplastics", the disclosures of which are incorporated herein by
reference) and blow molding processes (for example, that described in
Modern Plastics Encyclopedia/89, Mid October 1988 Issue, Volume 65,
Number 11, pp. 217-218, "Extrusion-Blow Molding", the disclosure of
30 which is incorporated herein by reference) and profile extrusion.
Some of the fabricated articles include sports articles, containers
such as for food or other household articles, footwear, automotive
articles, such as soft facia, sealants and assembly adhesives.

The compositions of the present invention can be further
35 combined with many thermoplastic polymers to improve their properties,
such as impact properties.

The compositions of the present invention are useful as tubing,
tapes, adhesives, film, wasters. The compositions of the present
invention are especially useful for the preparation of elastic films
40 and fibres, asphalt blends, wire and cable, sound barriers, wax

blends, pressure sensitive blends, and in the impact modification of thermoplastics.

The invention will be further illustrated by means of the following examples without limiting the invention thereto.

The compositions are defined by the following procedures.

Density is provided by the manufacturer or obtained by ASTM D 153.

Wt. Percent Styrene is obtained by ^1H NMR.

The following components are employed in the Examples and Comparative Experiments.

10 GENERAL PROCEDURE A FOR PREPARATION OF ETHYLENE/STYRENE COPOLYMERS A-E

Polymer is prepared in a 1 gallon agitated semi-continuous batch reactor. The reaction mixture generally consisted of a solvent comprising cyclohexane or isopar-8M and styrene. Prior to addition, solvent, styrene and ethylene are purified to remove water and oxygen. The inhibitor in the styrene is also removed. Inerts are removed by purging the vessel with ethylene. The vessel is then pressure controlled to a set point with ethylene. Hydrogen is added by filling a 70 cc cylinder to a set pressure and then adding it to the reactor to control molecular weight. Temperature in the vessel is controlled to set-point by varying the cooling flow of the cooling coils within the vessel. Prior to polymerization, the vessel is heated to the desired run temperature and the catalyst components: Titanium (N-1,1-dimethylethyl)dimethyl 1-(1,2,3,4,5- η -2,3,4,5,-tetramethyl-2,4-cyclopentadien-1-yl)silanimine (N,N)-dimethyl, CAS#135072-62-7, Tris(pentafluorophenyl)boron, CAS#101103-15-5, Modified methylaluminoxane Type 3A, CAS# 146905-79-5, are combined in mole ratios as shown and added to the vessel. After starting, the polymerization is allowed to proceed with ethylene supplied to the reactor as required to maintain vessel pressure. In some cases, hydrogen is added to the headspace of the reactor to maintain a mole ratio with respect to the ethylene concentration. At the end of the run, about 1,000 ppm of IrganoxTM 1010 anti-oxidant is then added to the solution on a polymer basis and the polymer is isolated from the solution by precipitation with methanol. The resulting polymers are dried in a vacuum oven. The following Table 1 contains the reactor conditions.

Table 1

Sample Number	Catalyst		Monomer		Reaction Conditions		Reactor Pressure		Reactor Temp	Polymer Yield g/g
	Time	Type	Time	Mon	Temp	Mon	Mon	Mon	Mon	g/g
E-1 - A	100	Isopar #3	100	100	100	100	100	100	100	100
E-2 - A	100	Isopar #3	100	100	100	100	100	100	100	100
E-3 - A	100	Isopar #3	100	100	100	100	100	100	100	100
E-4 - A	100	Isopar #3	100	100	100	100	100	100	100	100
E-5 - A	100	Isopar #3	100	100	100	100	100	100	100	100

Table 1 contd.

Sample Number	Zeit Flow Rate*	Weight Styrene Polymer	Catalyst conc. ratio Ti:B:Al	Catalyst Efficiency g poly/g Ti
E1 - A	100	10.0	1:100:1	100,000
E2 - B	100	10.0	1:100:1	100,000
E3 - C	100	10.0	1:100:1	100,000
E4 - D	100	10.0	1:100:1	100,000
E5 - E	100	10.0	1:100:1	100,000

* 100°C/1.1 kg

GENERAL PROCEDURE B FOR PREPARATION OF ETHYLENE/STYRENE COPOLYMERS F-H

5 ECI Catalyst dimethyl[N-(1,1-dimethylethyl)-1,1-dimethyl-1-(1,2,3,4,5-n)-1,5,6,7-tetrahydro-7-phenyl-s-indacen-1-yl]silanaminato(2-)-[N]-titanium. Preparation.

Preparation of 3,5,6,7-Tetrahydro-7-phenyl-s-indacen-1-yl-H₂-ene.

10 Indan (34.00 g, 0.254 moles) and 3-chloropropionyl chloride (100.99 g, 0.754 moles) were stirred in CHCl₃ (500 mL) at 0°C as AlCl₃ (130.00 g, 0.9750 moles) was added slowly under a nitrogen flow. The mixture was then allowed to stir at room temperature for 3 hours. The volatiles were then removed. The mixture was then cooled to 0°C and concentrated H₂SO₄ (500 mL) slowly added. The forming solid had to be frequently broken up with a spatula as stirring was lost early in this step. The mixture was then left under nitrogen overnight at room temperature. The mixture was then heated until the temperature readings reached 90°C. These conditions were maintained for a 2 hour period of time during which a spatula was periodically used to stir the mixture. After the reaction period crushed ice was placed in the mixture and moved around. The mixture was then transferred to a beaker and washed intermittently with H₂O and diethylether and then the fractions filtered and combined. The mixture was washed with H₂O (2 x 200 mL). The organic layer was then separated and the volatiles removed. The desired product was then isolated via recrystallization from hexane at 0°C as pale yellow crystals (22.36 g, 16.3% yield).

¹H NMR (CDCl₃): δ 2.04-2.19 (m, 2 H), 2.65 (s, 3 H), 2.84-3.0 (m, 4 H), 3.03 (s, 3 H), 5.5 (m, 1 H), 7.25 (s, 1 H), 7.33 (s, 1 H).

¹³C NMR (CDCl₃): δ 25.70, 26.01, 27.19, 33.04, 41.93, 118.40, 122.16, 135.98, 144.06, 152.84, 154.36, 156.50.

GC-MS: Calculated for C₁₇H₁₆O 172.09, found 172.05.

35 Preparation of 1,2,3,4-Tetrahydro-7-phenyl-s-indacen.

1,2,3,5-Tetrahydro-7-phenyl-s-indacene. 3H - no. 12.11 g, 0.06967 moles was stirred in methylene chloride (100 mL) and 1.7 g, 0.115 moles, 0.115 mL of 2.0 M solution in methylene chloride was added slowly. This mixture was then allowed to stir overnight at room temperature. After the reaction period the mixture was quenched by pouring over ice. The mixture was then acidified (pH 1) with HCl and stirred vigorously for 1 hour. The organic layer was then separated and washed with H₂O x 100 mL and then dried over MgSO₄. Filtration followed by the removal of the volatiles resulted in the isolation of the desired product as a dark oil (14.68 g, 80.3% yield).

¹H NMR (CDCl₃): δ 1.0-1.2 (m, 2 H), 1.8-3.1 (m, 4 H), 3.84 (s, 1H), 7.2-7.6 (m, 7 H).

GC-MS: Calculated for C₁₅H₁₅, 202.10, found 202.06.

15 Preparation of 1,2,3,5-Tetrahydro-7-phenyl-s-indacene, dilithium salt.

1,2,3,5-Tetrahydro-7-phenyl-s-indacene (11.05 g, 0.06967 moles) was stirred in hexane (100 mL) and nBuLi (0.069 moles, 10.00 mL of 2.0 M solution in cyclohexane) was slowly added. This mixture was then allowed to stir overnight. After the reaction period the solid was collected via suction filtration as a yellow solid which was washed with hexane, dried under vacuum, and used without further purification or analysis (12.2075 g, 91.13% yield).

Preparation of Chlorodimethyl(1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silane.

25 1,2,3,5-Tetrahydro-7-phenyl-s-indacene, dilithium salt (12.2075 g, 0.05102 moles) in THF (50 mL) was added dropwise to a solution of Me-SiCl₂ (12.5010 g, 0.1511 moles) in THF (100 mL) at 0°C. This mixture was then allowed to stir at room temperature overnight. After the reaction period the volatiles were removed and the residue extracted and filtered using hexane. The removal of the hexane resulted in the isolation of the desired product as a yellow oil (15.1492 g, 91.13% yield).

¹H NMR (CDCl₃): δ 0.33 (s, 3 H), 0.38 (s, 3 H), 2.20 (p, ³J_{HH}=7.5 Hz, 2 H), 2.9-3.1 (m, 4 H), 3.84 (s, 1 H), 6.69 (d, ³J_{HH}=2.8 Hz, 1 H), 7.3-7.6 (m, 7 H), 7.68 (d, ³J_{HH}=7.4 Hz, 2 H).

35 ¹³C NMR (CDCl₃): δ 0.24, 0.38, 26.28, 33.05, 33.18, 46.13, 116.42, 119.71, 127.81, 128.33, 128.64, 129.56, 136.51, 141.31, 141.86, 142.17, 142.41, 144.62.

GC-MS: Calculated for C₁₅H₁₅ClSi 324.11, found 324.06.

40

Preparation of N-(1,1-Dimethylethyl)-1,1-dimethyl-1-(1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silamine.

Dichlorodimethyl-1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silane (1.6517 g, 0.00247 moles) was stirred in hexane (100 mL) as NEt₃ (0.0123 g, 0.00471 moles) and t-butylamine (1.6374 g, 0.00665 moles) were added. This mixture was allowed to stir for 1 hour. After the reaction period the mixture was filtered and the volatiles removed resulting in the isolation of the desired product as a thick red-yellow oil (10.6551 g, 88.7% yield).

¹H NMR (CDCl₃): 10.12 (s, 1 H), 7.94 (s, 3 H), 7.27 (s, 3 H), 7.16 (p, 1 H, J_{HH}=7.2 Hz, 1 H), 6.7-6.9 (m, 4 H), 5.68 (s, 1 H), 4.69 (s, 1 H), 2.3-2.5 (m, 4 H), 2.03 (s, 1 H, J_{HH}=7.4 Hz, 1 H).

¹³C NMR (CDCl₃): -0.32, -0.09, 16.23, 33.32, 34.11, 46.46, 47.54, 49.81, 115.90, 119.30, 126.92, 127.99, 128.46, 132.99, 137.30, 140.20, 140.81, 141.03, 142.33, 144.53.

Preparation of N-(1,1-Dimethylethyl)-1,1-dimethyl-1-(1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silanimine, dilithium salt. N-(1,1-Dimethylethyl)-1,1-dimethyl-1-(1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silanimine (10.6551 g, 0.00247 moles) was stirred in hexane (100 mL) as nBuLi (0.070 moles, 35.00 mL of 2.0 M solution in cyclohexane) was added slowly. This mixture was then allowed to stir overnight during which time no salts crashed out of the dark red solution. After the reaction period the volatiles were removed and the residue quickly washed with hexane (2 x 50 mL). The dark red residue was then pumped dry and used without further purification or analysis (9.6517 g, 87.7% yield).

Preparation of Dichloro[N-(1,1-dimethylethyl)-1,1-dimethyl-1-((1,2,3,4,5-η)-1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silaminato(2-)-N]titanium.

N-(1,1-Dimethylethyl)-1,1-dimethyl-1-(1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silanimine, dilithium salt (4.5355 g, 0.01214 moles) in THF (50 mL) was added dropwise to a slurry of TiCl₄(THF)₂ (4.5005 g, 0.01214 moles) in THF (100 mL). This mixture was allowed to stir for 2 hours. PbCl₂ (1.7136 g, 0.006162 moles) was then added and the mixture allowed to stir for an additional hour. After the reaction period the volatiles were removed and the residue extracted and filtered using toluene. Removal of the toluene resulted in the isolation of a dark residue. This residue was then slurried in hexane and cooled to 0°C. The desired product was then isolated via filtration as a red-brown crystalline solid (2.9280 g, 43.5% yield).

1. 1994 年 12 月 31 日以前，在《公司法》施行前，已经依法设立的有限责任公司，其注册资本的实收率未达 80% 的，应当在 1995 年 6 月 30 日之前缴足；

[illegible][illegible][illegible]

45 Preparation of Dimethyl-[N-(1,1-dimethylethyl)-1,1-dimethyl-1-
1,2,3,4,5-naph-1,8,6,7-tetranydro-1-phenyl-1-indacen-1-
yl]diacetate 2-2-Titanium.

Sigillero (N- 1,1-dimethylpropyl- 1,1-dimethyl-1- 1,2,3,4,5-η -
 1,3,6,7-tetranydro-2-naphyl-1-indacen-1-yl)alluminato . - -titanium

0.4979 g, 0.001366 moles) was stirred in diethylether (30 mL) as MeMgBr (0.0021 moles, 0.70 mL of 3.0 M solution in diethylether) was added slowly. This mixture was then stirred for 1 hour. After the reaction period the volatiles were removed and the residue extracted and filtered using hexane. Removal of the hexane resulted in the isolation of the desired product as a golden yellow solid (0.4546 g, 66.7% yield).

¹H NMR (C₆D₆): δ 8.071 (s, 3 H), 7.49 (s, 3 H), 6.70 (s, 3 H), 6.73 (s, 3 H), 1.49 (s, 3 H), 1.7-1.8 (m, 2 H), 2.6-2.8 (m, 4 H), 6.41 (s, 1 H), 7.29 (s, CHH=7.1 Hz, 2 H), 7.48 (s, 1 H), 7.72 (d, CHH=7.4 Hz, 2 H), 7.92 (s, 1 H).

¹³C NMR (CDCl₃): 12.13, 14.61, 17.12, 22.86, 33.00, 41.73, 59.68, 63.62, 118.62, 121.98, 124.26, 127.32, 129.63, 128.98, 131.23, 134.39, 136.38, 143.19, 144.65.

35 Cocatalyst (bis(hydrogenated-tallowalkyl)methylamine) (B-FABA)
Preparation.

Methylcyclohexane (1200 mL) was placed in a 2L cylindrical flask. While stirring, bis(hydrogenated-tallowalkyl)methylamine (ARMEEN® M2HT, 104 g, ground to a granular form) was added to the flask and stirred until completely dissolved. Aqueous HCl 1N, 200 mL was added to the flask, and the mixture was stirred for 30 minutes. A white precipitate formed immediately. At the end of this time, $\text{LiB(C}_6\text{F}_5)_4 \cdot \text{Et}_2\text{O} \cdot 3 \text{ LiCl}$ MW = 687.3; 107.4 g was added to the flask. The solution began to turn milky white. The flask was equipped with a 6" Vigreux column topped with a distillation apparatus and the mixture was heated 140 °C external wall temperature. A

mixture of ether and methylcyclohexane was distilled from the flask. The two-phase solution was now only slightly milky. The mixture was allowed to settle at room temperature, and the contents were placed in a 1:1 separatory funnel. The aqueous layer was removed and discarded, and the organic layer was washed twice with H₂O and the aqueous layers again discarded. The saturated methylcyclohexane solutions were measured to contain 0.15 wt percent diethylether (Et₂O).

The solution (500 mL) was transferred into a 1 L flask, sparged thoroughly with nitrogen, and transferred into the drybox. The solution was passed through a column (1" diameter, 4" height) containing 13X molecular sieves. This reduced the level of Et₂O from 0.48 wt percent to 0.28 wt percent. The material was then stirred over fresh 13X sieves (20 g) for four hours. The Et₂O level was then measured to be 0.13 wt percent. The mixture was then stirred overnight, resulting in a further reduction in Et₂O level to approximately 10 ppm. The mixture was filtered using a funnel equipped with a glass frit having a pore size of 10-15 μ m to give a clear solution (the molecular sieves were rinsed with additional dry methylcyclohexane). The concentration was measured by gravimetric analysis yielding a value of 16.7 wt percent.

Polymerization

Ethylene/styrene copolymers F-H were prepared in a 6 gallon (22.7 L), oil jacketed, Autoclave continuously stirred tank reactor (CSTR). A magnetically coupled agitator with Lightning A-320 impellers provided the mixing. The reactor ran liquid full at 475 psig (3,275 kPa). Process flow was in at the bottom and out of the top. A heat transfer oil was circulated through the jacket of the reactor to remove some of the heat of reaction. At the exit of the reactor was a micromotion flow meter that measured flow and solution density. All lines on the exit of the reactor were traced with 50 psi (344.7 kPa) steam and insulated.

Ethylbenzene solvent was supplied to the reactor at 30 psig (207 kPa). The feed to the reactor was measured by a Micro-Motion mass flow meter. A variable speed diaphragm pump controlled the feed rate. At the discharge of the solvent pump, a side stream was taken to provide flush flows for the catalyst injection line (1 lb/hr = 0.45 kg/hr) and the reactor agitator (0.75 lb/hr = 0.34 kg/hr). These flows were measured by differential pressure flow meters and controlled by manual adjustment of micro-flow needle valves.

Uninhibited styrene monomer was supplied to the reactor at a rate of 1.17 gpa. The flow to the reactor was measured by a Micro-Motion mass flow meter. A variable speed diaphragm pump controlled the feed rate. The styrene stream was mixed with the remaining solvent stream. Ethylene was supplied to the reactor at 4.0 psig (1.137 kPa). The ethylene stream was measured by a Micro-Motion mass flow meter just prior to the research valve controlling flow. A Brooks flow meter/controller was used to deliver hydrogen into the ethylene stream at the outlet of the ethylene control valve. The ethylene hydrogen mixture combines with the solvent styrene stream at ambient temperature. The temperature of the solvent monomer as it enters the reactor was dropped to -60 °C by an exchanger with -120 glycol in the jacket. This stream entered the bottom of the reactor. The three component catalyst system and its solvent flush also entered the reactor at the bottom but through a different port than the monomer stream. Preparation of the catalyst components took place in an inert atmosphere glove box. The diluted components were put in nitrogen padded cylinders and charged to the catalyst run tanks in the process area. From these run tanks the catalyst was pressured up with piston pumps and the flow was measured with Micro-Motion mass flow meters. These streams combine with each other and the catalyst flush solvent just prior to entry through a single injection line into the reactor. Polymerization was stopped with the addition of catalyst kill (water mixed with solvent) into the reactor product line after the micromotion flow meter measuring the solution density. Other polymer additives can be added with the catalyst kill. A static mixer in the line provided dispersion of the catalyst kill and additives in the reactor effluent stream. This stream next entered post reactor heaters that provide additional energy for the solvent removal flash. This flash occurred as the effluent exited the post reactor heater and the pressure was dropped from 475 psig (3,275 kPa) down to ~250mm of pressure absolute at the reactor pressure control valve. This flashed polymer entered a hot oil jacketed devolatilizer. Approximately 85 percent of the volatiles were removed from the polymer in the devolatilizer. The volatiles exited the top of the devolatilizer. The stream was condensed with a glycol jacketed exchanger and entered the suction of a vacuum pump and was discharged to a glycol jacket solvent and styrene/ethylene separation vessel. Solvent and styrene were removed from the bottom of the vessel and ethylene from the top. The ethylene stream was measured with a Micro-Motion mass flow meter and analyzed for composition. The measurement of vented ethylene plus a calculation of the dissolved gases in the solvent/styrene stream

were used to calculate the ethylene conversion. The polymer separated in the devolatilizer was pumped out with a gear pump to a LDK-30 devolatilizing vacuum extruder. The dry polymer exits the extruder as a single strand. This strand was cooled as it was pulled through a water bath. The excess water was blown from the strand with air and the strand was chopped into pellets with a strand chopper.

The actual preparation conditions for each sample are summarized in Table 1.

Table 2

Sample	Reactor Temp C	Solvent Flow lb/hr	Ethylene Flow lb/hr	Hydrogen Flow lb/hr	Styrene Flow lb/hr	Conversion %	Catalyst	Co-Catalyst	B/Ti Ratio	MMAO ^d /Ti Ratio
E/S-F	91	31.49	2.4	7	7.8	88.9	CGC-7 ^b	B-FABA ^c	1.24	6
E/S-G	86.2	28.27	2.48	17	10.5	92.3	ES-1 ^a	B-FABA ^c	1.24	9.9
E/S-H	61.2	19.24	1.0	5	20.0	85.7	ES-1 ^a	B-FABA ^c	1.25	10

a ES1 catalyst is dimethyl[N-(1,1-dimethylethyl)-1,1-dimethyl-1-(1,1-dimethyl-1-(1,2,3,4,5-pentamethyl-1,3,5,6,7-tetrahydro-3-phenyl-5-indacen-1-yl)sulfonamido](2-)-N]-titanium.

b CGC-7 catalyst is (t-butylamido)(dimethyl-1,3,5,6,7-tetrahydro-1,1,3,3,5,5,6,6-octamethyl-1,3,5,6,7-tetrahydro-3-phenyl-5-indacen-1-yl)sulfonamido(2-)-N]-titanium.

Patent # 5,556,928, Example 17

c BFABA is bis-hydrogenated talloallyl methylammonium tetrakis (pentafluorophenyl) borate

d a modified methylaluminoxane commercially available from Akzo Nobel as MMAO-3A

ETHYLENE/STYRENE COPOLYMER A (41.1 wt percent; 32.5 mole percent styrene)

See General Procedure A. The resulting ethylene/styrene interpolymer had the following properties: weight percent styrene = 41.1; mole percent styrene = 32.5; density = 1.0982; melt flow rate (190°C, 2.2 Kg) = 1.77; heat of fusion = 3.6 J/g; glass transition temperature (DSC derived) = 17.2°C.

ETHYLENE/STYRENE COPOLYMER B (61.8 wt percent; 42.5 mole percent styrene)

See General Procedure A. The resulting ethylene/styrene interpolymer had the following properties: weight percent styrene = 61.8; mole percent styrene = 42.5.

ETHYLENE/STYRENE COPOLYMER C (64.1 wt percent; 42.5 mole percent styrene)

See General Procedure A. The resulting ethylene/styrene interpolymer had the following properties: weight percent styrene = 64.1; mole percent styrene = 42.5; density = 1.0982; melt flow rate (190°C, 2.2 Kg) = 1.34; glass transition temperature (DSC derived) = -4.6°C.

ETHYLENE/STYRENE COPOLYMER D (67.0 wt percent; 35.4 mole percent styrene)

See General Procedure A. The resulting ethylene/styrene interpolymer had the following properties: weight percent styrene = 67.0; mole percent styrene = 35.4; density = 1.0982; melt flow rate (190°C, 2.2 Kg) = 1.7; glass transition temperature (DSC derived) = -3°C.

ETHYLENE/STYRENE COPOLYMER E (72.5 wt percent; 41.6 mole percent styrene)

See General Procedure A. The resulting ethylene/styrene interpolymer had the following properties: weight percent styrene = 72.5; mole percent styrene = 41.6.

ETHYLENE/STYRENE COPOLYMER F (28.8 wt percent; 9.82 mole percent styrene)

See General Procedure B. The resulting ethylene/styrene interpolymer had the following properties: weight percent styrene = 28.8; mole percent styrene = 9.82; melt flow rate (190°C, 2.2 Kg) = 1.0. Further properties are shown in Table 1.

ETHYLENE-STYRENE COPOLYMER A is a copolymer having the following properties: weight percent styrene = 29.6; melt flow rate (200°C, 10 kg) = 10.6 g/10 min.

See General Procedure A. The resulting ethylene-styrene copolymer has the following properties: weight percent styrene = 29.6; melt flow rate (200°C, 10 kg) = 10.6. Further properties are known in Table 1.

ETHYLENE-STYRENE COPOLYMER B is a copolymer having the following properties: weight percent styrene = 29.6; melt flow rate (200°C, 10 kg) = 10.6.

See General Procedure B. The resulting ethylene-styrene copolymer has the following properties: weight percent styrene = 29.6; melt flow rate (200°C, 10 kg) = 10.6. Further properties are known in Table 1.

POLYOLEFIN A is a high density polyethylene available from The Low Chemical Company as POLYMER 100 having the following properties: density = 0.960 g/cm³; melt flow rate (200°C, 10 kg) = 12.4.

POLYOLEFIN B is an ethylene-butene copolymer available from The Low Chemical Company as POLYMER 100 having the following properties: density = 0.9178 g/cm³; melt flow rate (200°C, 10 kg) = 12.1.

BLOCK COPOLYMER A is VECTORTM 1011-D available from Dexco Polymers which is a Styrene-Isoprene-Styrene block copolymer containing 29.6 wt. percent styrene and 70.4 wt. percent isoprene having the following properties: melt flow rate (200°C, 10 kg) of 10.6 g/10 min.

BLOCK COPOLYMER B is VECTORTM 1006-D available from Dexco Polymers which is a Styrene-Butadiene-Styrene block copolymer containing 29.6 wt. percent styrene and 70.4 wt. percent isoprene having the following properties: melt flow rate (200°C, 10 kg) of 12.2 g/10 min.

BLOCK COPOLYMER C is VECTORTM 7400-D available from Dexco Polymers which is a Styrene-Butadiene-Styrene block copolymer with a molar ratio styrene/butadiene of 31.8/68.2 having the following properties: melt flow rate (200°C, 10 kg) of 17.3 g/10 min. and an oil content of 33.3 percent by weight.

BLOCK COPOLYMER D is KRATONTM G 1652 available from Shell Chemical Company which is a styrene-ethylene/butylene-styrene triblock copolymer containing 29.6 wt. percent styrene and 70.4 wt. percent ethylene/butylene.

EXAMPLES 1 - 3 AND COMPARATIVE EXPERIMENTS A - C

A. Preparation of Blend of Component A and Component B

A compression molding press (PHI Model CB234 D-X-MS-X21) was preheated to 300°C. A 7.0 gram portion of the blend consisting of stainless steel backing plates, TFE-coated glass film sheets, and a metal chase of approximately 44 mm high by 141 mm wide by 0.13 mm thick was prepared. Into the chase was evenly spread an amount of Block Copolymer pellets (Component A indicated in Table 1). From a slab of Component B was cut an amount of polymer indicated in Table 2 which was evenly distributed in the chase on top of the block polymer. A layered structure with TFE coated sheets was formed next to the polymer. The sandwich was preheated in the press at near minimum pressure for approximately one minute, then pressure of the press was increased to about 10,000 Kg of ram force for 10 seconds. The chase and the fused blend was removed when cooled to sufficient rigidity. The still warm blend was placed into an operating roll mill (155°C) for 2 minutes total. The blend was temporarily removed, folded, and replaced on the mill at least twice. The blend was removed from the roll mill and allowed to cool. This material was used for further fabrication.

B. Preparation of Test Sample

A compression molding press (PHI Model CB234 D-X-MS-X24) was preheated to 300°C. A 7.0 gram portion of the blend from A above was evenly distributed into a 75 mm wide by 115 mm high by 0.04 mm thick chase layered between TFE-coated glass sheets and metal backing plates. The following temperature program was followed: preheat 3.0 minutes at minimal pressure; medium force 0.5 minutes (10,000 Kg ram force); material cure 3.0 minutes (20,000 Kg ram force).

C. Preparation of Test Sample

A compression molded circle was prepared from another portion of the roll-milled blanket prepared in A above in a manner similar to the first sheet prepared in B above except that 14.0 grams of blend are used in a chase which has 76 mm diameter circles and which was approximately 0.1 mm thick. Circles are cut in half and coupled to required thickness for more A testing.

1. Tensile Properties Determined by Test

The test specimens are stored at 23°C for 24 hours or more prior to testing. Transmission haze was determined on the 1.01 mm sheets prepared in B above using a Hunterlab Tristimulus Colorimeter D50P-4 similar to ASTM D 1925. Tensile, modulus, and set specimens are determined by ASTM D 412. First and second tests. Tensile set protocol was 10 percent elongation, hold 10 seconds, return, wait 10 seconds, measure percent tensile set, defined as $\frac{\text{final gauge} - \text{initial gauge}}{\text{initial gauge}} \times 100$ where gauge was the length between grip jaws when force becomes apparent after removing slack.

Shore A hardness was determined by ASTM D 2240.

Force at 300 percent elongation, 300 percent modulus was determined by ASTM D 412.

Percent relaxation was as defined in ASTM D 412-94 after extension to 100 percent elongation and is based on force value upon reaching maximum elongation and after 30 seconds.

The test results are provided in Table 3.

Table 3

Blend #	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
	6252-5-8	6252-5-3	6252-5-19	6252-5-20	6252-5-4	6252-5-9	6252-5-15	6252-5-13
Component B	ES	ES	ES	ES	ES	ES	ES	ES
Type	Copolymer	Copolymer	Copolymer	Copolymer	Copolymer	Copolymer	Copolymer	Copolymer
	A	A	A	A	B	B	B	B
wt. % ethylene	55	55	55	55	48	48	48	48
wt. % styrene	45	45	45	45	52	52	52	52
Amount, grams	8	9	19	19	9	8	8	8
wt. %	20	20	50	50	20	20	20	20
Component A	Block Copolymer	Block Copolymer	Block Copolymer	Block Copolymer	Block Copolymer	Block Copolymer	Block Copolymer	Block Copolymer
Type	B	A	B	C	A	B	C	D
Amount, grams	32	36	19	19	36	32	32	31
wt. %	80	80	50	50	80	80	80	80
% Haze	23	17	53	60	28	33	65	98
Shore A Hardness	65	59	62	53	54	63	47	73
Ultimate Tensile								
psi	4,398	3,163	3,147	2,560	3,437	3,978	1,603	5,154
kPa	30,323	21,808	21,698	17,651	23,697	27,427	11,052	35,536
% Elongation at Break	850	925	542	758	1,017	858	1,092	558
Force at 300% Elongation(300% Modulus)								
psi	635	597	648	395	434	445	597	846
kPa	4,378	4,116	4,468	2,723	2,992	3,068	4,116	5,833
% Relaxation (after 150% elongation)	22	21	21	19	20	22	21	17
% Set (after 150% elongation)	11	11	13	13	10	12	13	11

Table 3 contd.

Bend #	Ex 9	Ex 10	Ex 11	Ex 12	Ex 13	Ex 14	Ex 15	Ex 16
	6252-5-5	6252-5-10	6252-5-21	6252-5-22	6252-5-6	6252-5-11	6252-5-16	6252-5-14
Component B	ES	ES	ES	ES	ES	ES	ES	ES
Type	Copolymer	Copolymer	Copolymer	Copolymer	Copolymer	Copolymer	Copolymer	Copolymer
wt. %ethylene	C	C	C	C	D	D	D	D
wt. %styrene	36	36	36	36	33	33	33	33
Amount, grams	64	64	64	64	67	67	67	67
wt. %	8	8	19	19	8	8	8	8
Component A	Block	Block	Block	Block	Block	Block	Block	Block
Type	Copolymer	Copolymer	Copolymer	Copolymer	Copolymer	Copolymer	Copolymer	Copolymer
Amount, grams	A	B	B	C	A	B	C	D
wt. %	32	32	19	19	32	32	31	32
	80	80	50	50	80	80	79	80
%Haze	73	89	99	99	78	84	99	99
Shore A Hardness	59	63	47	46	60	66	45	77
Ultimate Tensile								
ps	2,958	3,745	819	729	2,875	3,722	1,727	5,627
kPa	20,395	25,821	5,647	5,026	19,822	25,662	11,907	38,797
%Elongation at Break	900	742	1,000	1,050	958	733	983	468
Force at 300% Elongation(300% Modulus)								
ps	466	648	247	255	613	716	293	1,197
kPa	3,213	4,468	1,703	1,758	4,226	4,937	2,020	8,253
%Relaxation (after 150% elongation)	20	22	33	33	24	23	18	18
%Set (after 150% elongation)	12	10	18	17	12	12	17	10

Table 3 contd.

	Ex 17	Ex 18	Ex 19	Comp. Expt. A*	Comp. Expt. B*	Comp. Expt. C*	Comp. Expt. D*
Blend #	6252-5-5	6252-5-10	6252-5-21	6252-5-22	6252-5-6	6252-5-11	6252-5-16
Component B	ES Copolymer	ES Copolymer	ES Copolymer	Polyolefin	Polyolefin	Polyolefin	Polyolefin
Type	E	E	E	A	A	B	B
wt. % ethylene	27	27	27	---	---	---	---
wt. % styrene	73	73	73	---	---	---	---
Amount, grams	8	8	19	19	20	19	20
wt. %	20	20	50	50	50	50	50
Component A	Block Copolymer	Block Copolymer	Block Copolymer	Block Copolymer	Block Copolymer	Block Copolymer	Block Copolymer
Type	A	B	B	B	C	B	C
Amount, grams	32	32	19	19	20	19	20
wt. %	80	80	50	50	50	50	50
%Haze	88	83	99	94	93	99	99
Shore A Hardness	61	66	87	87	89	86	85
Ultimate Tensile							
psi	3,628	3,981	2,679	3,171	2,797	2,791	2,545
kPa	25,014	27,448	18,471	21,863	19,285	19,243	17,547
%Elongation at Break	958	783	417	842	750	742	717
Force at 300% Elongation(300% Modulus)							
psi	737	814	1,856	1,736	1,693	1,192	1,180
kPa	5,081	5,612	12,797	11,969	11,673	8,219	8,136
% Relaxation (after 150 elongation)	18	21	59	45	45	30	29
% Set (after 150% elongation)	11	12	62	63	59	40	39

* Not an example of the present invention.

EXAMPLES 20 - 26

5 a) Compression molding:

Samples were melted at 120 °C for 3 min and compression molded at 120°C under 20,000 lb of pressure for another 3 min. Subsequently, the molten materials were quenched in a press equilibrated at room temperature.

10 b) Differential Scanning Calorimetry (DSC):

A Du Pont DSC-2010 was used to measure the thermal transition temperatures and heat of transition for the samples. In order to

eliminate previous thermal history, samples were first heated to about 160 °C. Heating and cooling curves were recorded at 10 °C/min. Melting T_m from second heat and crystallization T_c temperatures were recorded from the peak temperatures of the endotherm and exotherm, respectively.

d) Dynamic Mechanical Spectroscopy (DMS):

Dynamic mechanical data were generated using a Rheometrics RSA-II solid state analyzer, and melt pressed (~10 mil thick) film test specimens. The DMS measurements were conducted at a step rate of 5 °C/min and a fixed frequency of 10 rad/sec. The glass transition temperature (T_g) of the samples was determined from the $\tan \delta$ peak maximum.

e) Shear Rheology:

Oscillatory shear rheology measurements were performed with a Rheometrics RMS-800 rheometer. Melt rheological properties were monitored at an isothermal set temperature of 120 °C in a frequency sweep mode, using parallel plate test geometry.

e) Mechanical Testing:

Tensile properties of the compression molded samples were measured using an Instron 1145 tensile machine equipped with an extensometer. ASTM-D638 samples were tested at a strain rate of 5 min^{-1} . Micro-tensile samples were tested at a speed of 5 in/min at -10 °C. The Young's Modulus (E, Mpa) measured was the average of four tensile measurements was given. The standard deviation for the ultimate properties was typically about 10 % of the reported average value. Also measured was the yield stress at the inflection point of the stress strain curve (σ_y , Mpa) and the Ultimate Tensile stress at break (σ_b , Mpa).

f) Tensile stress relaxation:

Uniaxial tensile stress relaxation was evaluated using an Instron 1145 tensile machine. Compression molded film (~20 mil thick) with a 10 mil gauge length was deformed to a strain level of 50% at a strain rate of 20 min^{-1} . The force required to maintain 50% elongation was monitored for 10 min. The magnitude of the stress relaxation was defined as S_r , the percentage = $(f_1 - f_2 / f_1) \times 100$ where f_1 was the initial force and f_2 was the final force.

g) Thermal Mechanical Analysis.

Upper service temperature (TMA(1mm)) was determined from a thermal mechanical analyzer (Perkin Elmer TMA 7 series) scanned at 5

0.5/min and a load of 1 Newton and defined as the point at which the probe penetrated 1 mm into the sample.

Example 20.

5 Example 20 was a blend containing 75 % by weight of ESI # F and 25 % by weight of Block Copolymer D. The blend was prepared by blending in a Haake Rheomix 6000 bowl mixer. The capacity of this mixer was 310 cc. Optimum volume for effective mixing was approximately 200 or 220 cc. Calculations were made considering
10 density and constituency of each component to prepare a dry blend of the materials to achieve a 10% volume fill. The dry blended materials were then added stepwise into the preheated calibrated bowl as the rotors were turning at 30 rpm. The materials were heated to approximately 150 degrees Centigrade. After a small melt heel was
15 established in the mixer, small increments of dry blend were added and allowed to melt and incorporate into the heel before more blend was added. This continued for approximately two minutes until all the blend was added. A sealing ram was then lowered on to the melt bowl and the melted blend was allowed to mix by roller blade action for an
20 additional ten minutes. At the end of this time the rotors were stopped, the mixer was dismantled, and the melt blend was removed and allowed to cool for further testing and analysis.

Example 21.

25 Example 21 was a blend containing 25 % by weight of ESI # F and 75 % by weight of Block Copolymer D. The blend was prepared essentially as for Example 20.

Example 22.

30 Example 22 was a blend containing 75 % by weight of ESI # G and 25 % by weight of Block Copolymer D. The blend was prepared essentially as for Example 20.

Example 13.

Example 13 was a blend containing 60 % by weight of ESI # G and 40 % by weight of Block Copolymer D. The blend was prepared essentially as for Example 10.

Example 14.

Example 14 was a blend containing 18 % by weight of ESI # G and 82 % by weight of Block Copolymer D. The blend was prepared essentially as for Example 10.

Example 15.

Example 15 was a blend containing 75 % by weight of ESI # H and 25 % by weight of Block Copolymer D. The blend was prepared essentially as for Example 20.

Example 16.

Example 16 was a blend containing 25 % by weight of ESI # H and 75 % by weight of Block Copolymer D. The blend was prepared essentially as for Example 20.

The properties of the various blends are summarized in Table 4. These data illustrate that as the mole % styrene content of the ESI component of the blend increases then the stress relaxation also increases. These data also illustrate that below approximately 22 mol % styrene content of the ESI component of the blend, as the styrene content of the ESI component of the blend decreases the Ultimate tensile value increases, whereas above approximately 22 mol % styrene content of the ESI component of the blend, as the styrene content of the ESI component of the blend increases, the Ultimate tensile value increases.

Table 4

Blend Components		I2	I10/I2	wt% dPS	mol% ^a	Tg (DSC) °C	Tm, °C	Tg (DMS) °C	Tg (LHS) °C	Tg (RHS) °C
E/S-F	ES29	1.0	7.7	5.8	9.82	-17.6	73.3	-4.7		
E/S-G	ES52	1.1	7.6	1.0	22.86	-11.9		-1.3		
E/S-H	ES75	2.2	9.2	8.6	42.50	20.6		30.6		
Block Copol. D							10.3	-43.4	101.2	
Blends		Components		Composn						
Ex 20	E/S-F/BC-D		(wt%)							
Ex 21	E/S-F/BC-D		75/25			-17.6	77.6	-46.7	-5.3	
Ex 22	E/S-G/BC-D		25/75				18.9/7 9.3	-44.5	-7.0	99.0
Ex 23	E/S-G/BC-D		75/25			-11.6		-45.1	-3.0	
Ex 24	E/S-G/BC-D		50/50			-10.3	15.8	-44.5	-3.0	100.1
Ex 25	E/S-H/BC-D		25/75					-44.5	0.9	101.2
Ex 26	E/S-H/BC-D		75/25			20.1		-42.3	30.0	
Ex 26	E/S-H/BC-D		25/75					-43.9	31.2	100.7

^amol% styrene = (wt% styrene/104)/((wt% styrene/104) + (wt% ethylene/98))

WHAT IS CLAIMED IS:

1 1. A thermoplastic elastomeric blend composition
2 comprising:
3 A) from 10 to 35 weight percent of a styrenic
4 block copolymer; and
5 B) from 1 to 35 weight percent of an interpolymers
6 of (i) at least one aliphatic α -olefin and (ii) at least one vinylidene
7 aromatic monomer or (B) a combination of at least one vinylidene
8 aromatic monomer and at least one hindered aliphatic vinylidene
9 monomer, wherein said vinylidene aromatic monomer is present in an
10 amount of from 0.5 to 15 mole percent or from 17 to 65 mole percent in
11 said interpolymers.
12

1 2. The composition of Claim 1 wherein the elastomer block
2 copolymer component (A) comprises at least one segment of a styrene
3 polymer and at least one segment of the following: isoprene polymer,
4 butadiene polymer, isoprene/butadiene copolymer, ethylene/butylene
5 copolymer or an ethylene/propylene copolymer; and component (B) is an
6 interpolymer of ethylene/styrene.

1 3. The composition of Claim 1 wherein the styrenic block
2 copolymer component (A) comprises a polystyrene-polyisoprene-
3 polystyrene or polystyrene-polybutadiene-polystyrene; and component
4 (B) is an interpolymer of ethylene/styrene.

5
1 4. The composition of Claim 1 wherein the styrenic block
2 copolymer component (A) contains from 10 to 35 weight percent of
3 styrenic polymer segments and from 90 to 65 weight percent of
4 elastomeric saturated olefin polymer segments, based on the total
5 weight of the block copolymer.

1 5. The composition of Claim 1 wherein the styrenic block
2 copolymer component (A) contains from 10 to 35 weight percent of
3 styrenic polymer segments and from 90 to 65 weight percent of
4 elastomeric unsaturated polydiene segments, based on the total weight
5 of the block copolymer.
1

1 4. The composition of claim 1, wherein component 3 has a
2 heat of fusion of less than 100 J/g.

1 5. The composition of claim 3 having a percent tensile
2 set after 10 percent elongation of 10 percent or less and a
3 transmission percent haze of 40 percent or less said haze value being
4 obtained on 0.04 mm thick sample.

1 6. A fabricated article made from the composition of
2 claim 1.

1 7. A fabricated article made from the composition of
2 claim 2.

1 8. A fabricated article made from the composition of
2 claim 3.

1 9. A fabricated article made from the composition of
2 claim 4.

1 10. A fabricated article made from the composition of
2 claim 5.

1 11. A fabricated article made from the composition of
2 claim 6.

1 12. A fabricated article made from the composition of
2 claim 7.

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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category: Citation of document with indication, where appropriate, of the relevant passages

Relevant to claim No.

X	WO 95 33006 A (DOW CHEMICAL CO) 7 December 1995 see page 13, line 26 - page 14, line 9	1-12
X	WO 95 26380 A (ADVANCED ELASTOMER SYSTEMS LOUHADI TRAZOLLAH (BE); HORRION JACQUES) 5 October 1995 * see page 7 line 32-35 * see page 9, line 14-26	1,4,5,8, 11,12
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-/-

☒ Further documents are listed in the continuation of box C

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X EP 0 641 536 A (GARDNER JOHN CHRISTOPHER
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1-12

INTERNATIONAL SEARCH REPORT

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MATIC MONOMER AND/OR HINDERED ALIPHATIC VINYLIDENE MONOMER INTERPOLYMER

(57) Abstract

A thermoplastic elastomeric blend composition comprising: (A) from 99 to 1 weight percent of a styrenic block copolymer; and (B) from 1 to 99 weight percent of an interpolpolymer of (1) at least one aliphatic α -olefin and (2) at least one vinylidene aromatic monomer or (3) a combination of at least one vinylidene aromatic monomer and at least one hindered aliphatic vinylidene monomer, wherein said vinylidene aromatic monomer is present in an amount of from 0.5 to 15 mole % or from 17 to 65 mole % in said interpolpolymer, and fabricated articles made from such composition.

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AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						